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TRANSMITTAL FORM

(to be used for all correspondence after initial filing)

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First Named Inventor	PETER GAMON JOHNS
Art Unit	TBD
Examiner Name	TBD
Attorney Docket Number	MSX-106(PCT/US)

ENCLOSURES (Check all that apply)

<input type="checkbox"/> Fee Transmittal Form	<input type="checkbox"/> Drawing(s)	<input type="checkbox"/> After Allowance Communication to TC
<input type="checkbox"/> Fee Attached	<input type="checkbox"/> Licensing-related Papers	<input type="checkbox"/> Appeal Communication to Board of Appeals and Interferences
<input type="checkbox"/> Amendment/Reply	<input type="checkbox"/> Petition	<input type="checkbox"/> Appeal Communication to TC (Appeal Notice, Brief, Reply Brief)
<input type="checkbox"/> After Final	<input type="checkbox"/> Petition to Convert to a Provisional Application	<input type="checkbox"/> Proprietary Information
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<input type="checkbox"/> Reply to Missing Parts under 37 CFR 1.52 or 1.53		

Remarks

1. Certified Copy of Priority Document - PCT/GB2004/050027
2. Certified Copy of Priority Document - GB 0326927.1
3. Certified Copy of Priority Document - GB 0513985.2
4. Return Receipt Postcard

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT

Firm Name	Kelley Drye & Warren LLP		
Signature			
Printed name	HANS-PETER G. HOFFMANN		
Date	JUNE 23, 2006	Reg. No.	37,352

CERTIFICATE OF TRANSMISSION/MAILING

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This collection of information is required by 37 CFR 1.5. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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The undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation and Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents held on an international application filed on **18 November 2004** under the Patent Cooperation Treaty at the UK Receiving Office. The application was allocated the number **PCT/GB2004/050027**.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in the certificate and any accompanying documents has re-registered under the Companies Act 1985 with the same name as that with which it was registered immediately before re-registration, for the substitution as, or the inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

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Date: May 9, 2006

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PCT REQUEST

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0	For receiving Office use only	
0-1	International Application No.	PCT/GB 2004 / 0 5 0 0 2 7
0-2	International Filing Date	18 NOVEMBER 2004 18-11-04
0-3	Name of receiving Office and "PCT International Application"	United Kingdom Patent Office PCT International Application
0-4	Form - PCT/RO/101 PCT Request	
0-4-1	Prepared Using	PCT Online Filing Version 3.50 (Build 0001.162)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	United Kingdom Patent Office (RO/GB)
0-7	Applicant's or agent's file reference	
I	Title of Invention	SILVER SOLDER OR BRAZING ALLOYS AND THEIR USE
II	Applicant	
II-1	This person is:	applicant only
II-2	Applicant for	all designated States except US
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II-9	Facsimile No.	n/a
II-10	e-mail	n/a

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III-1	Applicant and/or inventor	
III-1-1	This person is:	applicant and inventor
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III-1-4	Name (LAST, First)	JOHNS, Peter, Gamon
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V	DESIGNATIONS	
V-1	The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents.	
VI-1	Priority claim of earlier national application	
VI-1-1	Filing date	19 November 2003 (19.11.2003)
VI-1-2	Number	0326927.1
VI-1-3	Country	GB
VII-1	International Searching Authority Chosen	European Patent Office (EPO) (ISA/EP)

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VIII	Declarations	Number of declarations	
VIII-1	Declaration as to the identity of the inventor	—	
VIII-2	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	—	
VIII-3	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	—	
VIII-4	Declaration of inventorship (only for the purposes of the designation of the United States of America)	1	
VIII-5	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	—	

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VIII-4-1	<p>Declaration: Inventorship (only for the purposes of the designation of the United States of America) Declaration of Inventorship (Rules 4.17(iv) and 51bis.1(a)(iv)) for the purposes of the designation of the United States of America:</p>	<p>I hereby declare that I believe I am the original, first and sole (if only one inventor is listed below) or joint (if more than one inventor is listed below) inventor of the subject matter which is claimed and for which a patent is sought.</p> <p>This declaration is directed to the international application of which it forms a part (if filing declaration with application).</p> <p>I hereby declare that my residence, mailing address, and citizenship are as stated next to my name.</p> <p>I hereby state that I have reviewed and understand the contents of the above-identified international application, including the claims of said application. I have identified in the request of said application, in compliance with PCT Rule 4.10, any claim to foreign priority, and I have identified below, under the heading "Prior Applications", by application number, country or Member of the World Trade Organization, day, month, and year of filing, any application for a patent or inventor's certificate filed in a country other than the United States of America, including any PCT international application designating at least one country other than the United States of America, having a filing date before that of the application on which foreign priority is claimed.</p>
VIII-4-1-1	Prior applications:	

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		<p>I hereby acknowledge the duty to disclose information that is known by me to be material to patentability as defined by 37 C.F.R. § 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the PCT international filing date of the continuation-in-part application.</p> <p>I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.</p>
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VIII-4-1-1-2	Residence: (city and either US State, if applicable, or country)	Watford, United Kingdom
VIII-4-1-1-3	Mailing address:	39 Richmond Drive Watford, Hertfordshire WD1 3BQ United Kingdom
VIII-4-1-1-4	Citizenship:	GB
VIII-4-1-1-5	Inventor's Signature: (if not contained in the request, or if declaration is corrected or added under Rule 26ter after the filing of the international application. The signature must be that of the inventor, not that of the agent)	/Peter Johns/
VIII-4-1-1-6	Date: (of signature which is not contained in the request, or of the declaration that is corrected or added under Rule 26ter after the filing of the international application)	18 November 2004 (18.11.2004)

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IX	Check list	number of sheets	electronic file(s) attached
IX-1	Request (including declaration sheets)	6	✓
IX-2	Description	22	✓
IX-3	Claims	2	✓
IX-4	Abstract	1	✓
IX-5	Drawings	1	✓
IX-7	TOTAL	32	
	Accompanying Items	paper document(s) attached	electronic file(s) attached
IX-8	Fee calculation sheet	—	✓
IX-17	PCT-SAFE physical media	—	—
IX-19	Figure of the drawings which should accompany the abstract	1	
IX-20	Language of filing of the international application	English	
X-1	Signature of applicant, agent or common representative	/Claire Hodson/	
X-1-1	Name (LAST, First)	Claire Hodson (Director)	
X-1-2	Name of signatory		
X-1-3	Capacity		
X-2	Signature of applicant, agent or common representative	/Peter Gamon/	
X-2-1	Name (LAST, First)	JOHNS, Peter, Gamon	
X-2-2	Name of signatory		
X-2-3	Capacity		
X-3	Signature of applicant, agent or common representative	/Paul Cole/	
X-3-1	Name (LAST, First)	COLE, Paul, Gilbert	
X-3-2	Name of signatory		
X-3-3	Capacity		

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10-1	Date of actual receipt of the purported international application	18 NOVEMBER 2004 18-11-04
10-2	Drawings:	✓
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/EP
10-6	Transmittal of search copy delayed until search fee is paid	

FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by the International Bureau	
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SILVER SOLDER OR BRAZING ALLOYS AND THEIR USE

FIELD OF THE INVENTION

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The present invention relates to silver solder or brazing alloys and to their use in making soldered joints in various grades of silver, particularly silversmithing grades. Silver brazing alloys are also known in the silversmithing trade as silver solders or solders and these terms are used interchangeably herein.

10

BACKGROUND TO THE INVENTION

Various silver-based alloys of the silver-copper-zinc type are useful as solders (brazing materials). Brazing has been defined as a joining process in which
15 a filler metal is used which has a melting point of above 450°C, but below that of the parent metal and which is distributed in the joint by capillary attraction.

Silver, copper and zinc form a ternary eutectic with a silver content of 56% and melting at 665°C, see a ternary phase diagram which is given in Fig. 2 of
20 Jacobson et al, *Development of new silver-free brazing alloys for steel tubular assembly*, supplement to the Welding Journal (sponsored by the American welding Society/Welding Research Council), August 2002, pages 149-S to 155-S downloadable from <http://www.aws.org/wj/supplement/08-2002-JACOBSON-s.pdf>. A commercially supplied silver alloy recommended by the AWS for brazing
25 mild steel or copper has the composition of 44 wt % Ag, 30 wt % Cu and 26 wt % Zn. Such an alloy has too low silver content for use in silversmithing, where solder alloys of at least 55 wt % Ag are the norm.

Depending on their melting temperatures, brazing alloys for use in
30 silversmithing are classified as Easy, Medium and Hard, and the major UK suppliers quote the values below:

Thessco	Solidus	Liquidus
Easy	705°C	725°C
Medium	720°C	765°C
Hard	745°C	778°C

5

Johnson Matthey	Solidus	Liquidus
Easy	705°C	723°C
Medium	720°C	765°C
Hard	745°C	778°C

10

An alloy containing 75 wt % Ag, 22 wt % Cu and 3 wt % Zn is known and provides a good colour match for silver, but is high melting. An alloy with 70 wt % Ag, 20 wt % Cu and 10 wt % Zn is also of good colour and is lower melting, and a further alloy containing 65 wt % Ag, 20 wt % Cu and 15 wt % Zn is still lower melting, see <http://www.wlv.com/joining/silvabrazrefchart.xls>. This is, of course, only one web page from one of the various suppliers of solder alloys for silversmiths.

A corrosion-resistant silver solder for use in the electronics industry is disclosed in JP 61078592 (Kyocera) and is based on Ag, 0.05-19 wt %, Ge, 0.01-1.0 wt % Pd, and 0.01-2 wt % Li. An exemplified composition contains Ag 94 wt %, Ge 4 wt %, Pd 0.5 wt %, Li 0.5 wt %, Fe 0.5 wt % and Ni 0.5 wt %, and another exemplified composition has Ag 80%, Ge 11.95%, Pd 8% and Li 0.05%. Recommended amounts of germanium are relatively high. For silversmithing, the use of palladium is to be avoided, as is the use of lithium even in trace amounts. Although spreadability and wettability are said to be desirable properties, colour match to the material being soldered is not necessary.

Patent GB-B-2255348 (Rateau, Albert and Johns; Metaleurop Recherche) discloses a novel silver alloy that maintains the properties of hardness and lustre inherent in Ag-Cu alloys while reducing problems resulting from the tendency of the copper content to oxidise. The alloys are ternary Ag-Cu-Ge alloys containing at least

92.5 wt% Ag, 0.5-3 wt % Ge and the balance, apart from impurities, copper. Patents US-A-6168071 and EP-B-0729398 (Johns) disclose a silver/germanium alloy which comprises a silver content of at least 77 wt % and a germanium content of between 0.4 and 7%, the remainder principally being copper apart from any impurities, which alloy contains elemental boron as a grain refiner at a concentration of greater than 0 ppm. and less than 20ppm. Silver alloys according to the teaching of GB-B-2255348 and EP-B-0729398 are now commercially available in Europe and in the USA under the trade name Argentium (Ag 92.5 wt%, Cu 6.3 wt%, Ge 1.2 wt %), and the word "Argentium" as used herein refers to these alloys.

SUMMARY OF THE INVENTION

In one aspect the invention provides a silver solder alloy of the Ag-Cu-Zn family containing at least 55 wt % Ag and from 0.5 to 3 wt % Ge.

The above alloys can exhibit an advantageous combination of relatively low melting point, high flowability and good colour. In particular, such alloys may have a solidus temperature in the range of about 700 to about 750°C and a liquidus temperature in the range of about 725°C to about 780°C. They can be used for soldering or brazing jewellery metals including grades of silver such as Sterling. They are particularly advantageous for soldering Argentium silver.

Other preferred features of the invention will be apparent from the appended claims to which attention is directed. The alloys may contain 1.5-2.5 wt % Ge, especially 2.0-2.5 wt % Ge and more especially about 2.0 wt % Ge. Addition of Ge has been found to improve colour and reduce melting point as well as to increase corrosion resistance.

The Ag-Cu-Zn alloy typically contains 55-77 wt % Ag, 10-30 wt% Cu (preferably 56-75 wt %) and 8-15 wt % Zn. For flowability, it may further comprise 0.05-0.4 wt % Si especially about 0.1-0.2 wt % Si. Too large a proportion gives rise to brittleness. The alloy may further comprise 1-3 wt % Sn, especially about 2

wt % Sn which again reduces melting point and improves colour. It may further comprise an amount of boron of e.g. 1 ppm-0.3 wt % boron, and more typically 0.1-0.3 wt % of boron which reduces grain size and helps in rolling or drawing the composition.

5

Particular compositions comprise:

(a) 55-77 wt % Ag, 10-30 wt % Cu and 8-15 wt % Zn, 2-2.5 wt % Ge and 0.05-0.4 wt % Si,

(b) 55-77 wt % Ag, 10-30 wt % Cu and 8-15 wt % Zn, 2-2.5 wt % Ge and 1-
10 3 wt % Sn, or

(c) 55-77 wt % Ag, 10-30 wt% Cu and 8-15 wt% Zn, 2-2.5 wt % Ge, 0.05-0.4 wt % Si and 1-3 wt % Sn.

The alloys of the invention may be provided any form that is convenient for
15 silversmithing, e.g. rod, strip, wire, fine particles or a paste in which powdered metal is suspended in a vehicle, and may be used with conventional fluxes. In the case of pastes, US-A-5443658 (Hermanek) discloses a vehicle which is an aqueous gel containing 78 weight percent water, 10 weight percent mineral oil, 10 weight percent glycerin with the balance sodium carboxymethyl-cellulose. US-A-5120374
20 (Mizuhara) discloses gels containing 1-4 wt. % hydroxypropylcellulose, 40-80 wt. % 1,2-propanediol, 18-58 wt. % 2-propanol or 1-4 wt. % hydroxypropylcellulose, 20-70 wt. % 1,2-propanediol, 26-76 wt. % water. US-A-4475959 discloses an organic vehicle system based on resins dispersed in hydroxylic solvents. Low-melting hydrocarbon vehicles may also be used. Useful materials include those
25 melting below room temperature to normally solid materials, e.g. C₁₈-C₆₀ petroleum hydrocarbon waxes melting from 28°C. to 100°C. Such materials should have a low ash or solid residue content and either melt and flow, sublime and/or thermally decompose below 500°C. Useful hydrocarbons may be paraffinic, aromatic, or
30 mixed aromatic paraffinic or mixtures of compounds of such characteristics, and include various mixtures of hydrocarbons, e.g., octadecane, mineral spirits, paraffin wax, and petrolatum (a colloidal system of non-straight-chain solid paraffinic

hydrocarbons and high boiling liquid paraffinic hydrocarbons, in which most of the liquid hydrocarbons are held inside the micelles), e.g., Vaseline.

The alloys can be used in any conventional soldering or brazing method e.g. using a hand torch, a fixed burner, induction or resistance heating or using a brazing furnace, preferably such a furnace which provides a protective atmosphere.

The invention is further illustrated in the following examples

10

Example 1

A brazing composition was prepared by melting together the following materials:

	Ag	-	58%
15	Ge	-	2%
	Sn	-	2.5%
	Zn	-	14.5%
	Si	-	0.1%
	Cu	-	22.9%.

The resulting composition rolled well from cast ingot (satisfactory to 40% work hardened, then required annealing) and was evaluated as being a good solder when tested initially on gilding metal samples. The solder composition runs well along a 'T' join. Compared to known 56 and 60 silver solders (56 and 60 wt % Ag), the observed colour was good, and in particular it compared favourably to that of the 60 solder. On tarnish testing the present solder appeared brighter than the 56 and 60 solders. Its melting point on gilding metal using a Degussa flux was below that of the conventional 56 silver solder.

Samples of Argentium Ag/Ge supplied by Thessco Ltd of Sheffield were soldered using the above solder composition and the conventional 56 and 60 silver solder and using various fluxes:

Degussa Flux – the melting point of the above composition was slightly below that of the 60 silver solder. Beading of the solder was observed before dispersion. The resulting soldered joint exhibited good surface texture.

5 Superior 601 flux – The melting point of the above composition was lower than using the Degussa Flux and no beading of the solder was observed before dispersion. The resulting joint exhibited good surface texture.

10 Thessco Y Flux - The melting point of the above composition was lower than with either the Degussa Flux or the Superior 601 flux and was observed to be the same as the 56 silver solder. No beading of solder before dispersion was observed, and the resulting soldered joint exhibited good surface texture when tested alongside the 60 silver solder but gave a slightly rough joint at the melting temperature of the 65 silver solder suggesting that a slightly
15 higher temperature would be preferable.

The present solder was evaluated as being one of the best for use at relatively low temperatures. Its advantages and disadvantages were as follows:

- 20
- Good colour in comparison to other lower M.P. solders including standard 56 silver solder.
 - Lowest M.P. in comparison to the other solders produced.
 - Solder runs well along a 'T' join.
 - Good results in tarnish test carried out at Thessco Ltd. - the solder of this
25 Example was brighter than both 56 and 60 solders after test.
 - Surface of solder a little rough on some of the Argentium (Thessco) samples (soldering temperature may have needed to have been pushed a little higher with these samples).

Example 2

30

A brazing composition was prepared by melting together the following materials:

7

	Ag	-	58%
	Ge	-	2%
	Sn	-	-
	Zn	-	14%
5	Si	-	0.1%
	Cu	-	25.9%

The resulting composition rolled well from cast ingot and provided a good solder that when tested on gilding metal samples was of good colour and ran well along a 'T' joint. However its melting point was above that of the 60 silver solder.

10 When using Thessco F flux, beading of the solder before dispersion was observed, but the same beading occurred with the 60 silver solder.

Example 3

15 A brazing composition was prepared by melting together the following materials:

	Ag	-	65%
	Ge	-	2%
	Sn	-	-
20	Zn	-	9%
	Si	-	0.1%
	Cu	-	23.9%

The resulting composition rolled well from cast ingot and provided a good solder when tested on gilding metal samples but its colour was slightly yellow.

25 When using Thessco F flux, the melting point was slightly above that of known "Easy" silver solder and beading of the solder before dispersion was observed. Beading was also observed with Superior flux 6. Using Superior flux 601, the melting point was the same as that of Easy silver solder and beading of the solder before dispersion was not observed.

Example 4

5 A brazing composition was prepared by melting together the following materials:

	Ag	-	58%
	Ge	-	2%
	Sn	-	-
10	Zn	-	14%
	Si	-	0.4%
	Cu	-	25.6%

The resulting composition rolled well from cast ingot and provided a good solder that when tested on gilding metal samples was of good colour. Its melting
15 point was closely below that of the 60 silver solder. When soldered onto a flat surface of gilding metal, the surface texture exhibited was slightly rough.

Example 5

20 A brazing composition was prepared by melting together the following materials:

	Ag	-	58%
	Ge	-	2%
	Sn	-	-
25	Zn	-	17%
	Si	-	0.4%
	Cu	-	24.6%

The resulting composition exhibited a yellow colour and was not evaluated
further.

A brazing composition was prepared by melting together the following
5 materials:

10	Ag	-	56%
	Ge	-	2%
	Sn	-	-
	Zn	-	19.8%
	Si	-	0.2%
	Cu	-	22%

15 **Example 7**

A brazing composition was prepared by melting together the following materials:

20	Ag	-	65%
	Ge	-	2%
	Sn	-	-
	Zn	-	13.5%
	Si	-	0.1%
	Cu	-	19.2%

Example 8

30 A brazing composition was prepared by melting together the following materials:

10

	Ag	-	67%
	Ge	-	2%
	Sn	-	-
	Zn	-	8%
5	Si	-	0.1%
	Cu	-	22.9%

The resulting composition rolled well from cast ingot and provided a very good solder when evaluated using Thessco F flux on gilding metal samples. It exhibited good colour and no beading of the solder before dispersion. The composition exhibited a melting point slightly above that of Easy silver solder. However, when re-tested on Argentium Ag/Ge material (Thessco) using Degussa flux it exhibited a slightly better colour and a lower melting point than Easy silver solder. When soldering a 'T' joint in Argentium feeding the solder with a stick and using a Degussa flux the solder flowed very well. The present solder was judged to be one of the best for use at higher soldering temperatures because of the following advantages:

- Rolled well from cast ingot.
- M.P. slightly lower than that of Example 10
- Solder runs very well along a 'T' joint.
- Good colour.
- Good surface texture.

Example 9

A brazing composition was prepared by melting together the following materials:

	Ag	-	60%
	Ge	-	2%
	Sn	-	-
30	Zn	-	13%
	Si	-	0.1%
	Cu	-	24.9%

The resulting composition rolled well from cast ingot and provided a very good solder when tested initially on gilding metal samples. It exhibited good colour and when using Degussa flux, no beading of the solder was observed before dispersing. Using Thessco F flux, beading of the solder before dispersion was observed, but known 60 silver solder also beaded on the same gilding metal sample. The above solder composition runs well along a 'T' joint and provides good surface texture. Its melting point is fractionally above that of known 60 silver solder. When soldered onto Argentium (Thessco), the colour was fairly good and the solder appeared greyer than Easy solder.

Example 10

A brazing composition was prepared by melting together the following materials:

Ag	-	70%
Ge	-	2%
Sn	-	-
Zn	-	8%
Si	-	0.1%
Cu	-	19.9%

The resulting composition rolled well from cast ingot and provided a very good solder when evaluated initially on gilding metal samples. When using Degussa flux no beading of the solder was observed before dispersion, but beading was observed using Thessco F flux. The solder exhibited good surface texture and had a melting point slightly lower than Easy. When tested on Argentium (Thessco) using Degussa flux, its melting point was slightly higher than that of the solder of Example 8, but its colour was slightly better. The present composition was judged to be one of the best for use at higher soldering temperatures because of the following advantages:

- Rolled well from cast ingot.
- Good colour match with Argentium - slightly better colour than Example 8.

- M.P. slightly lower than Easy.
- Solder runs well along a 'T' joint.
- Generally good surface texture.

5

Example 11

A brazing composition was prepared by melting together the following materials:

	Ag	-	56%
10	Ge	-	2%
	Sn	-	-
	Zn	-	13%
	Si	-	0.2%
	Cu	-	28.8%

15 The resulting composition rolled well from cast ingot and provided a good solder as evaluated on gilding metal samples, with good colour and good surface texture. The solder ran well along a 'T' join using Thessco flux. Also using Thessco flux, a large section of gilding metal spinning was soldered onto a base without any problems and with good solder flow. A sample was tested alongside 56 silver solder
20 using different fluxes and was found to have a higher melting point. With Thessco F flux, both the present solder composition and the 56 silver solder exhibited beading before dispersion, whereas with Degussa flux beading results varied between samples.

25

Example 12

A brazing composition was prepared by melting together the following materials:

	Ag	-	74%
30	Ge	-	2%
	Sn	-	-
	Zn	-	8%

13

Si	-	0.1%
Cu	-	15.9%

The resulting composition rolled well from cast ingot and provided a good solder as evaluated on gilding metal samples, with good colour and good surface texture. The solder ran well along a 'T' joint using Thessco flux. Its melting point was slightly lower than Easy silver solder and fractionally lower than the solder of Example 10. Using Thessco F flux, beading of the solder before dispersion was observed but the resulting joint had good surface texture. When tested on Argentium (Thessco) an excellent colour match was achieved and the same melting temperature as Easy silver solder was obtained but with incomplete dispersion, suggesting that a higher melting temperature is desirable.

Example 13

A brazing composition was prepared by melting together the following materials:

Ag	-	60%
Ge	-	3%
Sn	-	-
Zn	-	12%
Si	-	0.1%
Cu	-	24.9%

The resulting composition had a melting point lower than known 56 silver solder but did not roll well from cast ingot.

Example 14

A brazing composition was prepared by melting together the following materials:

Ag	-	60%
Ge	-	2.5%
Sn	-	-

14

Zn	-	12.5%
Si	-	0.1%
Cu	-	24.9%

- 5 The resulting composition rolled quite well from cast ingot (satisfactory to 40% work hardened, then required annealing).

Example 15

- 10 A brazing composition was prepared by melting together the following materials:

	Ag	-	60%
	Ge	-	2.5%
	Sn	-	-
15	Zn	-	12.5%
	Si	-	0.1%
	Cu	-	24.9%

- The resulting composition rolled quite well from cast ingot (satisfactory to 40% work hardened, then required annealing) and exhibited good colour. Samples
20 tested on gilding metal alongside known 56 and 60 silver solders using different fluxes exhibited beading before dispersion.

Example 16

- 25 A brazing composition was prepared by melting together the following materials:

	Ag	-	74%
	Ge	-	2%
	Sn	-	1%
30	Zn	-	7.5%
	Si	-	0.2%
	Cu	-	15.3%

The resulting composition rolled well from cast ingot and exhibited good colour but its melting point was higher than Easy solder and than the solder of Example 12, and it does not disperse fully.

5

Example 17

A brazing composition was prepared by melting together the following materials:

10	Ag	-	74%
	Ge	-	2%
	Sn	-	-
	Zn	-	13%
	Si	-	0.2%
	Cu	-	10.8%

15 The resulting composition did not roll well from cast ingot. It was tested initially on gilding metal using Degussa Flux and exhibited better colour and a reduced melting point compared to Easy.

Example 18

20

A brazing composition was prepared by melting together the following materials:

25	Ag	-	74%
	Ge	-	2%
	Sn	-	-
	Zn	-	13%
	Si	-	-
	Cu	-	11%

30 The resulting composition rolled quite well from cast ingot (satisfactory to 40% work hardened, then required annealing). Solder tested initially on gilding metal using Degussa flux exhibited good colour and a lower melting point than Easy silver solder. When tested on Argentium (Thessco) Ag/Ge material alongside

Easy silver solder, the present composition exhibited lower melting point and after polishing provided a better colour match to the Argentium, making the Easy silver solder look yellow. When tested on Argentium using Degussa flux alongside the solder of Example 10, the melting point was similar or slightly lower and the colour match after polishing was slightly darker. When tested on Argentium using Degussa flux, the solder ran well along a T-joint. The present solder was judged to be one of the best for use at higher temperatures for the following reasons:

- Solder does not contain Si (one less constituent to add to the alloy).
- M.P. fractionally lower than that of Example 10 (as seen with sample 2).
- Solder runs well along a 'T' joint.
- Good surface texture.
- Rolled well from cast ingot.

Example 19

A brazing composition was prepared by melting together the following materials:

Ag	-	58%
Ge	-	2%
Sn	-	2.5%
Zn	-	14.5%
Si	-	-
Cu	-	23%

The resulting composition was the same as Example 1 except that the silicon was omitted. It rolled quite well from cast ingot (satisfactory to 40% work hardened, then required annealing). When tested on Argentium (Thessco) material alongside 56 silver solder using Degussa flux, it ran well along a T-joint, exhibited a melting point slightly higher than 56 silver solder, and exhibited better colour. When tested on samples of Argentium (Thessco) alongside the solder of Example 1 using Degussa the melting point was unchanged, the colour became fractionally more yellow and the solder did not disperse so well.

Example 20

A brazing composition was prepared by melting together the following materials:

5

Ag	-	74%
Ge	-	2%
Sn	-	1%
Zn	-	11.4%
Si	-	0.2%
Cu	-	11.4%

10

The resulting composition was a very hard alloy, very brittle when rolled from cast ingot and yellow in colour in comparison to Easy silver solder.

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Example 21

A brazing composition was prepared by melting together the following materials:

20

Ag	-	68%
Ge	-	2%
Sn	-	2%
Zn	-	8%
Si	-	0.1%
Cu	-	19.9%

25

The resulting composition rolled well from cast ingot, exhibited a melting point slightly lower than Easy silver solder, and good colour, although it was slightly more yellow than Easy silver solder.

Example 22

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The brazing composition of Example 21 was re-melted with 3 wt % added tin. The resulting composition rolled not as well as that of Example 21: it rolls down to 40%

then becomes brittle. Its melting point was lower than the composition of Example 21, showing that addition of tin lowers the melting point, and its melting point was lower than that of 60 silver solder. Its colour was yellow compared to Easy solder, but it flowed well using F flux.

5

Example 23

A brazing composition was prepared by melting together the following materials:

10	Ag	-	58%
	Ge	-	2%
	Sn	-	1.4%
	Zn	-	14.5%
	Si	-	0.1%
15	Cu	-	24%

The resulting composition rolled better than the solder of Example 1, illustrating that tin additions tend to make silver solders harder and more brittle. When soldered onto gilding metal using Thessco F flux, the present composition had a melting point lower than 60 silver solder but beaded before dispersing. The 20 56 silver solder also beaded at the same time as the present solder but dispersed before the present solder. When soldered onto Argentium using F flux, the present solder dispersed well, melted fractionally below 56 silver solder and exhibited slightly better colour than that solder.

25

Example 24

A brazing composition was prepared by melting together the following materials:

5	Ag	-	69%
	Ge	-	2%
	Sn	-	2%
	Zn	-	8%
	Si	-	0.1%
10	Cu	-	18.9%

The resulting composition rolled well from cast ingot but melted at a temperature significantly higher than easy silver solder. When soldered onto Argentium (Thessco), both solders beaded before dispersion when heated from above but dispersed without beading when heated from below.

15

Example 25

A brazing composition was prepared by melting together the following materials:

20	Ag	-	58%
	Ge	-	2%
	Sn	-	2.5%
	Zn	-	14.5%
	Si	-	0.1%
25	B	-	0.14%
	Cu	-	22.76%

The resulting composition (which was the same as that of Example 1 except for the addition of boron) rolled well from cast ingot (edge cracking at 64% reduction). When soldered onto Argentium (Thessco) using Thessco F flux it melted below 56 silver solder but higher than Thessco MX12 silver solder, exhibited similar colour to the solder of Example 1 and dispersed well. This solder

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composition was evaluated as being one of the joint best for low temperature uses, and it had the following advantages:

- Addition of boron allows the alloy to roll better than the solder of Example 1.
- 5 • M.P. lower than 56 solder.
- Good colour in comparison to other lower M.P. solders including standard 56 silver solder.

A comparison of tarnish resistance was carried out using 'hard' and 'easy' silver solders together with the solder of this example (Y solder). Hard, Easy and Y solders were soldered onto Argentium Silver. The soldered samples were polished using two types of polishing compounds, then degreased using a solvent cleaner in an ultrasonic cleaning tank and finally wiped with a silver polishing cloth. An accelerated tarnishing procedure was carried out by exposing the samples to neat ammonium polysulphide solution - 20% for 10 minutes. After 10 minutes exposure, the Y solder showed superior tarnish resistance in comparison to both the hard and easy silver solders as shown in Fig. 1, which gives photographs of the samples.

Example 26

20

A brazing composition was prepared by melting together the following materials:

	Ag	-	63%
	Ge	-	2%
25	Sn	-	1%
	Zn	-	14%
	Si	-	0.1%
	B	-	0.14%
	Cu	-	19.76%

30 The resulting composition rolled well from cast ingot (edge cracking at 60% reduction) and when soldered using F flux onto Argentium (Thessco) had a melting point significantly lower than 60 silver solder. It exhibited a melting point between

the solders of Examples 10 and 25, a better colour than 56 or 60 silver solders and beading on one sample tested but not on the other. It was considered the best solder composition for use at medium temperatures because of its combination of rolling properties, melting point and colour.

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Example 27

A brazing composition was prepared by melting together the following materials:

10	Ag	-	63%
	Ge	-	2%
	Sn	-	-%
	Zn	-	15%
	Si	-	0.1%
15	B	-	0.14%
	Cu	-	19.76%

The resulting composition (which was the same as Example 26 apart from the absence of tin) rolled well from cast ingot (edge cracking at 75% reduction). When soldered onto Argentium (Thessco) using Thessco F flux it exhibited a melting point higher than that of the solder of Example 26, showing the effect of Sn in reducing the melting point.

20

Example 28

A brazing composition was prepared by melting together the following materials:

25	Ag	-	58%
	Ge	-	2%
	Sn	-	2.5%
30	Zn	-	14.5%
	Si	-	-%
	B	-	0.14%

Cu - 22.86%

The resulting composition which was the same as Example 25 except for the absence of silicon) did not roll well from cast ingot (edge cracking at 32% reduction) and appeared yellow. It was believed that the mold temperature used was too yellow, and on re-melting with a higher mould temperature the resulting cast ingot rolled better with edge cracking at 57% reduction.

Example 29

A brazing composition was prepared by melting together the following materials:

Ag	-	58%
Ge	-	2%
Sn	-	2.5%
Zn	-	14.5%
Si	-	0.3%
B	-	0.14%
Cu	-	22.56%

The resulting composition rolled fairly well from cast ingot (edge cracking at 50% reduction).

CLAIMS

1. A silver solder or brazing alloy of the Ag-Cu-Zn family containing at least
5 55 wt % Ag and from 0.5 to 3 wt% Ge.
2. The alloy of claim 1, containing 1.5-2.5 wt % Ge.
3. The alloy of claim 1, containing about 2 wt % Ge.
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4. The alloy of any preceding claim, containing 55-77 wt % Ag, 10-30 wt% Cu
and 8-15 wt% Zn.
5. The alloy of any preceding claim, further comprising 0.05-0.4 wt % Si.
15
6. The alloy of claim 5, comprising about 0.1 wt% Si.
7. The alloy of any preceding claim, further comprising 1-3 wt % Sn.
- 20 8. The alloy of claim 7, comprising about 2 wt % Sn.
9. The alloy of any preceding claim, containing 55-77 wt % Ag, 10-30 wt% Cu
and 8-15 wt% Zn, 2-2.5 wt % Ge and 0.05-0.4 wt % Si.
- 25 10. The alloy of any preceding claim, containing 55-77 wt % Ag, 10-30 wt% Cu
and 8-15 wt% Zn, 2-2.5 wt % Ge and 1-3 wt % Sn.
11. The alloy of any preceding claim, containing 55-77 wt % Ag, 10-30 wt% Cu
and 8-15 wt% Zn, 2-2.5 wt % Ge, 0.05-0.4 wt% Si and 1-3 wt % Sn.
30
12. The alloy of any preceding claim, further comprising 0.1-0.3 wt % boron.

13. The alloy of any preceding claim having a solidus temperature of about 705°C and a liquidus temperature of about 725°C.
14. The alloy of any of claims 1-12, having a solidus temperature of about 720°C and a liquidus temperature of about 765°C.
15. The alloy of any of claims 1-12, having a solidus temperature of about 745°C and a liquidus temperature of about 778°C
16. Use of the alloy of any preceding claim to solder or braze a joint in silver.
17. Use of the alloy of any of claims 1-15 to solder or braze a joint in Sterling silver.
18. Use of the alloy of any of claims 1-15 to solder or braze a joint in silver of content about Ag 92.5 wt%, Cu 6.3 wt%, Ge 1.2 wt %.
19. An alloy according to any of claims 1-15, which is in the form of rod, strip or wire.
20. An alloy according to any of claims 1-15, which is in the form of paste.

ABSTRACT**SILVER SOLDER OR BRAZING ALLOYS AND THEIR USE**

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The present invention relates to silver solder or brazing alloys and to their use in making soldered joints in various grades of silver, particularly silversmithing grades. They alloys are of the Ag-Cu-Zn family containing at least 55 wt % Ag and from 0.5 to 3 wt% Ge. They can exhibit an advantageous combination of colour,

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flowability and corrosion resistance.

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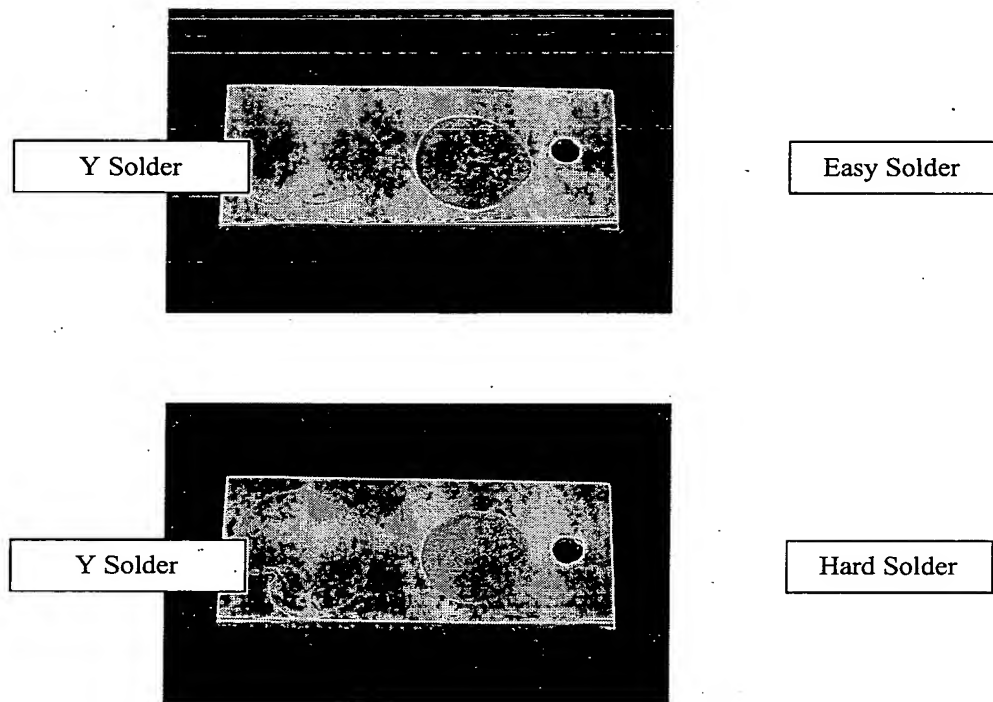


Fig. 1

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